Evaluation of Vadose Zone and Source Modules for Multi-media, Multi-pathway, and Multi-receptor Risk Assessment Using Large-Soil-Column Experimental Data

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Abstract

The United States Environmental Protection Agency (EPA) is developing a comprehensive environmental exposure and risk analysis software system for potential agency-wide application using the methodology of a Multi-media, Multi-pathway, Multi-receptor Risk Assessment (3MRA) model. This software system will have application to the technical assessment of exposures and risks relevant for national waste management rules to protect the health of humans and other living organisms. Evaluation of the suitability and applicability of the component modules used for 3MRA is critical. The Ground Water and Ecosystem Restoration Division (GWERD) of EPA's National Risk Management Research Laboratory previously conducted a large-soil-column study to investigate the behavior of organic pollutants, including halogenated aliphatic hydrocarbons, substituted benzenes, and phenols, during infiltration of municipal wastewater into soil. Based on a feasibility study, the data from this study were used to directly evaluate two modules of 3MRA: the LAU (Land Application Units) source module and the VZ (Vadose Zone) module. The Generic Soil Column sub-module, which is a fundamental component for LAU, waste piles, and landfills, was also evaluated indirectly through the evaluation of the LAU source module. Moreover, since the LAU and VZ modules are sequentially implemented in the 3MRA model, the overall performance of the two combined modules was evaluated. In general the LAU and VZ modules function quite well in simulating the fate and transport of organic constituents in source areas and vadose zones, although noticeable differences were observed between the simulated and observed results for highly volatile organics. Finally, the ways for enhancing appropriate applications of those modules are suggested.

Key Words: Model evaluation, land application units, organic compounds, vadose zone, volatilization.

Introduction

The United States Environmental Protection Agency (EPA) is developing a comprehensive environmental exposure and risk analysis software system for potential agency-wide application using the methodology of a Multi-media, Multi-pathway, Multi-receptor Risk Assessment (3MRA) model (U.S. EPA, 2003). This software system will have application to the technical assessment of exposures and risks relevant for national waste management rules to protect the health of humans and other living organisms. Evaluation of the suitability and applicability of the component modules used for 3MRA is critical. The Ground Water and Ecosystem Restoration Division (GWERD) of EPA's National Risk Management Research Laboratory (NRMRL) previously conducted a large-soil-column study to investigate the behavior of organic pollutants, including halogenated aliphatic hydrocarbons, substituted benzenes, and phenols, during infiltration of municipal wastewater into soil (Piwoni at al., 1986). Based on a feasibility study, the data from this study were used to directly evaluate two modules of 3MRA: (1) the LAU (Land Application Units) source module and (2) the VZ (Vadose Zone) module. The Generic Soil Column sub-module (GSCM), which is a fundamental component for Land Application Units (LAU), waste piles, and landfills, was also evaluated indirectly through the evaluation of the LAU source module. Acceptability of the LAU module would imply the acceptability of the GSCM sub-module. Since the LAU and VZ modules are sequentially implemented in the 3MRA model, the overall performance of the two combined modules was also evaluated.

The LAU source module simulates the fate and transport of the vapor phase, the liquid phase and the solid phase. Mechanisms modeled include constituent mass balance, gas phase losses from soil to air by volatilization, advective or diffusive leaching of aqueous phase constituent mass from the bottom of the waste management units, and first order losses from abiotic- and bio- degradation. The LAU source module was used to simulate the top portion of the laboratory microcosm where volatilization of organic compounds occurred. Aspects of the evaluation of the LAU source module included: 1) Whether volatilization of organic constituents could be correctly accounted for; 2) An evaluation of whether the concepts of different attributes of the module such as boundary conditions and the assumption of first order decay for chemical transformation are adequate, and whether the quasi-analytical approach employed for solving the

mathematical model to describe the flow, fate and transport is appropriate; 3) Whether the LAU thickness and temperature parameters have significant effects on the amount of volatilization of organics; and 4) Whether suggestions on how to appropriately apply the LAU module could be made through the evaluation.

The VZ module is used to simulate the fate and transport of contaminants leaching from a land-based waste management unit through the underlying vadose zone. It performs one dimensional water flow and contaminant transport using analytical and numerical solutions. The module simulates contaminant transport by advection and dispersion with linear or nonlinear sorption. However, fate and transport in the gas phase are not accounted for in the VZ module. Aspects of the evaluation of the VZ module included: 1) Whether modeling without accounting for the gas phase could acceptably describe the chemical fate and transport processes in the vadose zone; 2) Whether the assumption of first order decay of chemical transformation is valid; 3) An evaluation of whether the conceptualizations of different attributes of the VZ module such as boundary conditions, and the mathematical model to describe the flow, fate and transport as well as its solutions are adequate; and 4) Whether suggestions on how to appropriately apply the VZ module could be made through the evaluation.

Design and Data Set Outline of the GWERD Large Column Soil Experiment

Data from an earlier microcosm study of the behavior of organic pollutants during rapid infiltration of municipal wastewater (Piwoni, et al., 1986) offered an opportunity to evaluate two modules of 3MRA. In this earlier study glass columns with a 15 cm I.D. and a 150 cm length were filled with a fine sandy soil obtained from a site near Ada, Oklahoma. A solution of municipal wastewater dosed with a mixture of organic chemicals was applied to the columns at four-hour intervals. The columns were sampled through a series of probes along their length. In addition, the columns, which are shown in Figure 1, were constructed in a manner that allowed a direct measurement of volatilization and facilitated a mass balance to allow estimates of contaminant transformation. For details on the construction of the columns and the operation of the study, please see Piwoni, et al. (1986). The average water content of the fine sandy soil was measured to be 0.21. Its porosity was 0.4. The saturated hydraulic conductivity of the soil was estimated as 3.47 cm/h. During this Lab experiment, 20 ^{o}C temperature with 2 ^{o}C fluctuation was maintained. In addition, 0.733 cm of wastewater was applied every 4 hours. The chemical compounds examined included halogenated aliphatic hydrocarbons, substituted benzenes, phenols, and miscellanies.

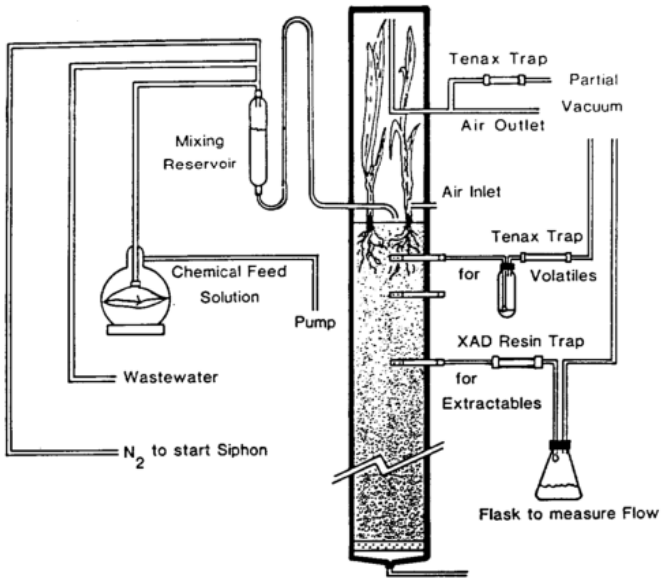

Figure 1 Design of the GWERD large soil column study to simulate the fate and transport of organic contaminants in municipal wastewater applied to soil. (After Piwoni et al., 1986).

Procedure and Methodologies for Evaluation

For the LAU module evaluation, an individual standalone LAU program was obtained by modifying the LAU module from the 3MRA model to meet the requirements of small intervals of time and space for utilization of the lab experiment data. This LAU program was implemented to fulfill evaluations of the LAU module after the consistency of the LAU program to the original LAU module was examined. The necessary parameters to implement the LAU program were obtained from the lab experimental design and literature review. Comparison of the simulated and the observed volatilization rates provides a basis for evaluating the application of the LAU module. In addition, the simulation outputs of leachate concentration were used as input to the VZ module, the results from which were compared with the lab experimental data to assess the overall errors from sequential applications of both the LAU and VZ modules. Sensitivity analyses were implemented to examine the effect of thickness and temperature parameters of the LAU module on the evaluation. Furthermore, the evaluation was performed based on the chemical categories and the volatility of organic compounds. Through the comparisons and result analyses, the suitability and applicability of the LAU module to the designed lab experiment scenarios, which could represent a typical land treatment operation, and the technical soundness of the module would be evaluated.

For the VZ module evaluation an individual standalone VZ program was obtained by modifying the VZ module from the 3MRA model to meet the requirements of small intervals of time and space as well as outputs for any depths along the soil column for utilization of the lab experiment data. This VZ program was implemented to fulfill evaluations of the VZ module after the consistency of the VZ program to the original VZ module was examined. The necessary parameters to implement the VZ program were obtained from the lab experimental design, literature review, and parameter calibrations. Concentrations of organic compounds of interest at selected sampling ports were compared with the model simulation results. It was further evaluated by taking the calibrated first-order transformation rates obtained based on the concentrations from part of the sampling ports. Then model verifications were carried out using the concentration data from the other sampling ports. We call this procedure a "dual step" approach -- parameter calibrations using partial data with followed validations. Furthermore, comparisons were performed between the simulation results from the evaluated VZ module and the other tested and accepted models with similar or enhanced functions such as CHEMFLO in order to investigate the VZ compatibility with those models. Moreover, the evaluation was performed based on the chemical categories and the volatility of organic compounds. Through the comparisons and result analyses, suitability and the applicability of the VZ module to the designed lab experiment scenarios, which could represent a typical field infiltration, and the technical soundness of the module would be evaluated.

Simulation Scenarios and Specifications of Input Parameters

LAU Module

The LAU module assumes that waste is applied to the soil surface at even intervals and tilled to a zone of fixed depth. Upon each application of waste the till zone is completely mixed and the total contaminant mass in the till zone is increased by the added amount. The contaminant partitioning to three phases, adsorbed, dissolved and gaseous, is at instantaneous, reversible equilibrium. Flow and transport of contaminants in the vertical direction of the till zone are modeled by GSCM (the Generic Soil Column Module), which assumes zero concentration at the upper boundary while providing choices of either zero concentration or zero gradient at the lower boundary.

The laboratory microcosm experiment applied wastewater at intervals of every 4 hours and at a flux of 4.4 cm/day. As suggested by the researcher conducting the experiment (Enfield et al., 1982), each application of wastewater would replace 3.5 cm of soil solution if the water content of soil remained at 0.21. Therefore, flow conditions in the top portion of the microcosm seem to agree with the LAU assumption of complete

initial mixing. Meanwhile, air in the head space of the microcosm was flushed at a rate to replace it very eight minutes, which approximates the LAU assumption of zero concentration at the upper boundary.

This study models the top 7.5 cm of the microcosm as a land application unit (LAU) with 2910 waste applications per year. Zero concentration gradient is chosen for the lower boundary, although it is different from the experimental condition of non-zero concentration gradient.

The soil column of the LAU zone with total thickness of 0.075m was discretized into 375 layers, each of 0.2mm. Layer thickness was specified small enough that the time interval was not greater than the length of time between mass additions (waste applications). In addition, the time step was determined so that it was equal to the convection time of chemicals passing each layer to completely get rid of the numerical dispersion. Thus, the time step was equal to the layer thickness divided by the effective velocity. To reduce numerical errors that could be evaluated through a mass balance check, a small layer thickness was specified for the soil column flow and transport simulations.

VZ Module

The vadose zone model integrates a 1-D flow sub-module with a 1-D transport sub-module. The flow sub-module employs Darcy's law (Freeze and Cherry, 1979) and the transport sub-module implements an advection-dispersion equation proposed by Huyakorn and Pinder (1983). A linear sorption assumption was employed for the transformation of organics. It should be noted that for transport solutions, a semi-analytical approach was applied, and a semi-infinite column was assumed with concentration equal to zero at infinite depth for organic constituents. The average water content that was obtained through several points with varied depths along a soil column and the effective velocity are used to acquire the flow and transport solutions. Although the vadose zone module in 3MRA model does not have the capability to directly compute the concentration for a organic constituent at the depths other than the bottom of a soil column, it is possible for the modified VZ model to obtain the concentration at any depths by specifying the water content equal to that calculated from a case with the total thickness of the simulated vadose zone. Due to the limited sample numbers at the upper three ports (port 1, 2 & 3) at depths of 7.5, 15, and 30 cm, average values of concentrations from the three ports were employed to approximately represent the concentration at the depth of 15 cm. Therefore, the thickness of vadose zone for simulating the soil column in the GWERD study was the remaining 135cm.

The VZ standalone program requires five input files: the head file hd.ssf, the site-layout file sl.ssf, the chemical and physical loading (i.e. infiltration and leach flux) file sr.grf, the vadose zone specific input file vz.ssf, and the chemical properties file cp.ssf. To date, in the VZ module evaluation, four chemical compounds, PCE, 1,1,1-TCA, Bis- (2-chloroethyl) ether, and 1,2-Dibromo-3-Chloropropane, have been examined. The transformation decay rate for 1,2-Dibromo-3-Chloropropane was specified either based on a literature review or through calibrations. Please note that the average of the observed concentrations from the Lab data were applied to the model evaluations so that the effect of the variation of sample concentrations could be significantly reduced or eliminated.

Evaluation Results

LAU Module

Figure 2 shows a comparison of the simulated and the observed volatilization rate. The error bars show the 95% confidence intervals of the experimental observations. For halogenated aliphatic hydrocarbons, which are highly volatile, the simulated values are significantly smaller; but the general trend of higher volatilization at higher Henry's law constant is followed and the results are in the same order of magnitude. Good matches are achieved for substituted benzenes, which undergo both volatilization and biodegradation.

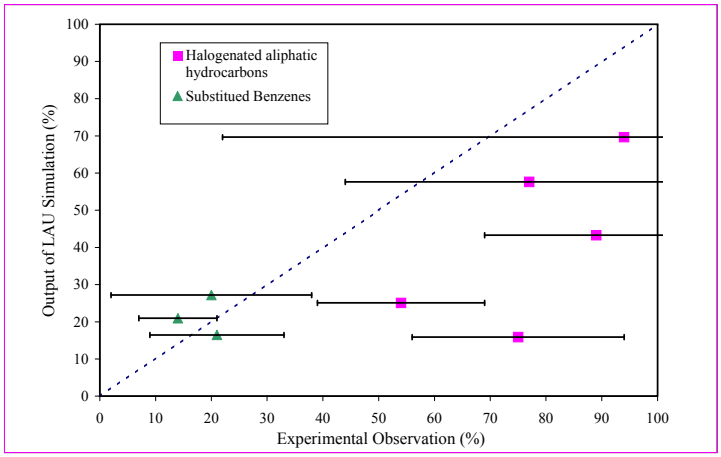

Fig. 2 Comparison of the simulated and the observed volatilization rate.

Table 1 lists simulation outputs for all studied compounds, including those whose volatilization rates were not directly measurable from the experiment and were reported as calculated values (Piwoni et al., 1986). Model outputs well approximate the calculated values for low-volatile compounds such as phenol, 2-chlorophenol, bis(2-chloroethyl) ether, nitrobenzene and 1,2-dibromo-3-chloropropane.

The results show that the volatilization rate modeled by the LAU module is the right order of magnitude for all categories of compounds involved in the experiment. It suggests that the LAU module, or at least the GSCM, can be used with a considerable confidence to obtain reasonable results.

In order to test model sensitivity to the thickness of the till zone, simulations were run for one compound from each chemical category at four different till zone thickness: 0.035 m, 0.075 m, 0.15m and 0.30m. It is observed that the simulated volatilization rate changed only slightly when the LAU thickness changed by almost an order of magnitude. With the increase of thickness, a very small increase is observed for compound with high volatilization and very slow transformation, while a bigger increase is observed for compound with significant rate of transformation (biodegradation), such as toluene and chlorobenzene.

Because temperature has a significant impact on chemical properties that affect volatilization and it is reported that temperature fluctuated from 18 to 22^{o}C in the experiment (Piwoni at al., 1986), simulations were run at 15, 18, 20, 22 and 25 ^{o}C. The 3MRA chemical database was used to obtain the chemical properties for these compounds at the corresponding temperatures. The calculation of chemical properties at different temperature is automatic when the compound of interest is included in the 3MRA database. The absolute values of the volatilization rate increased by no more than 5% for chlorinated hydrocarbons and 10 to 17% for chlorobenzene and toluene, when temperature increased from 15 to 22 ^{o}C. The results show that the LAU module has the capability of reflecting the effect of minor changes in temperature.

Table 1. Comparison between the simulated and the observed volatilization rates for all studied compounds.

	Volatilization Rate (Percent)	
Compounds	Reported	Simulated by LAU
Halogenated aliphatic hydrocarbons		
Chloroform	75±19	16
1,1-dichloroethane	54±15	25
1,1,1-trichloroethane	89±20	43
Trichloroethene	77±33	58
Tetrachloroethene	94±72	70
1,2-dibromo-3-chloropropane	6[a]	3[c]
Substituted benzenes		
chlorobenzene	14±7	21[c]
1,2-dichlorobenzene	21±12	16[c]
Toluene	20±18	27[c]
nitrobenzene	<0.1[b]	0.1[c]
Phenols		
phenol	<0.1[b]	0.01[d]
2-chlorophenol	<0.2[b]	0.2[d]
Misc.		
bis(2-chloroethyl) ether	3[b]	0.1

Notes:
[a] calculated value due to coelution with other compounds (Piwoni et al., 1986).
[b] calculated value due to inability to measure directly (Piwoni et al., 1986).
[c] assume first-order biodegradation rate of 0.2 day^{-1}.
[d] assume first-order biodegradation rate of 0.21 day^{-1}.

VZ Module

Figures 3 through 6 show the comparisons between the model results and Lab data for the concentration of the four chemical compounds.

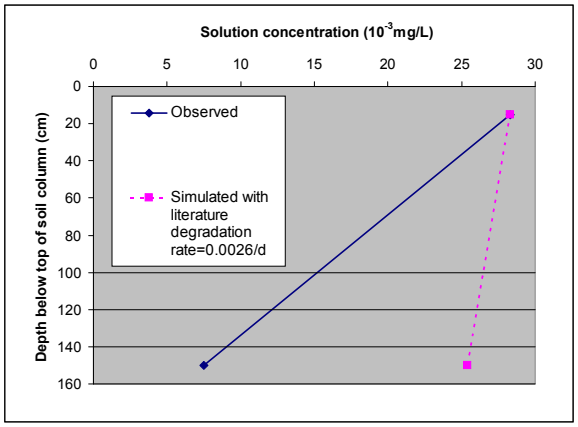

Fig. 3 Comparisons between observed and simulated chemical concentrations (PCE) for Vadose Zone module.

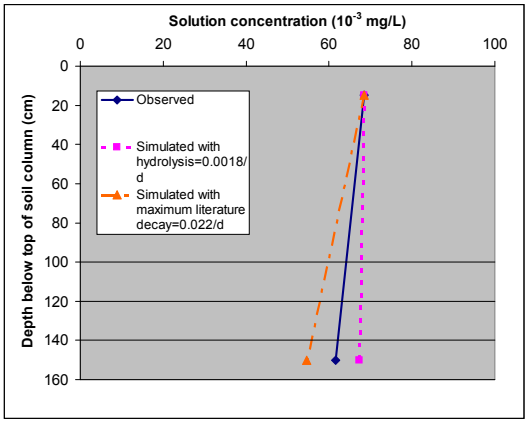

Fig. 4 Comparisons between observed and simulated chemical concentrations (1,1,1-TCA) for Vadose Zone module.

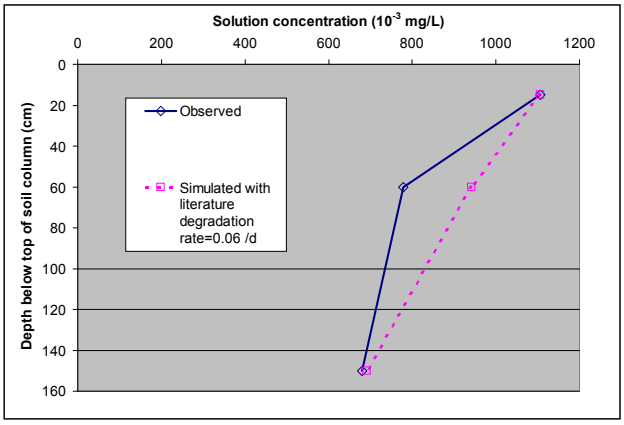

Fig. 5 Comparisons between observed and simulated chemical concentrations (Bis- (2-chloroethyl) ether) for Vadose Zone module.

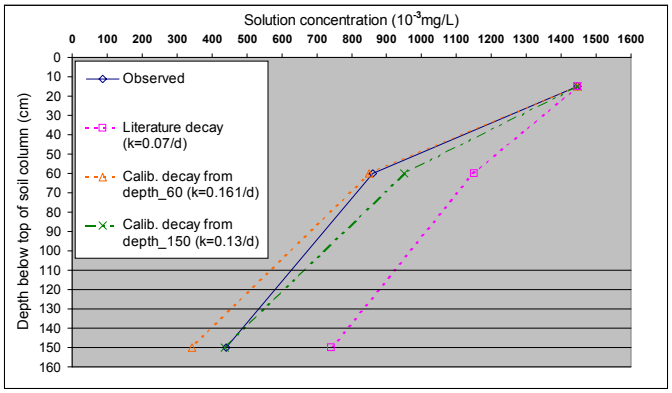

Fig. 6 Comparisons between observed and simulated chemical concentrations (1,2-Dibromo-3-Chloropropane) for Vadose Zone module.

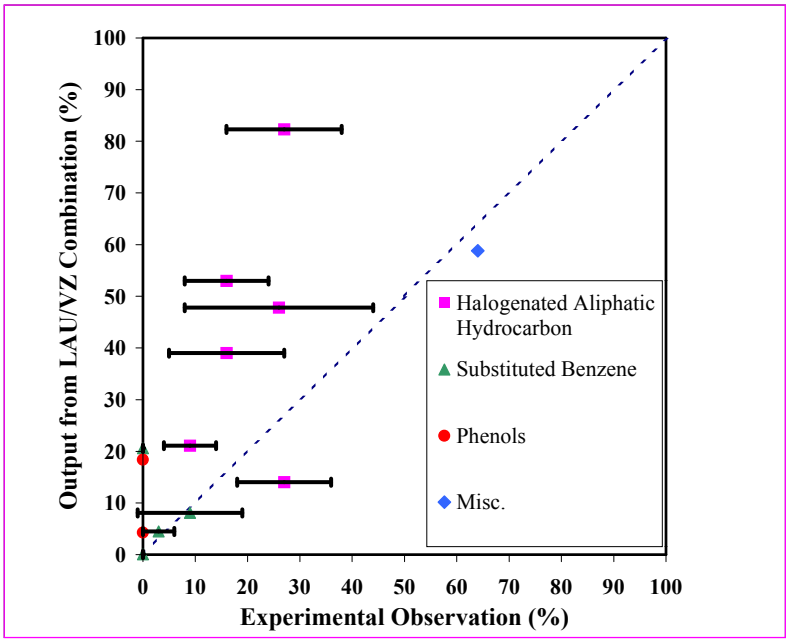

Fig. 7 The simulated and the observed solute retaining rate (ratio of effluent concentration to influent concentration).

Overall Evaluation of Ending Output through both LAU and VZ Modules

The simulated and the observed solute retention rates (ratio of effluent concentration to influent concentration) are plotted against each other in Figure 7. The error bars show the 95% confidence intervals of the experimental observations. For all halogenated aliphatic hydrocarbons except 1,1-dichloroethane, model outputs are significantly larger than observations. Such is expected since the LAU module underestimates the volatilization and a very little amount of chemical is transformed in the VZ module. For substituted benzenes, the results are relatively good. The simulated values match observations very well for

chlorobenzene, toluene, and 1,1-dichlorobenze, but are larger than the observation for nitrobenzene, which may be attributed to an inaccurate input of the biodegradation rate constant. A good fit is also observed for bis(2-chloroethyl) ether. For phenol and 2-chlorophenol, the simulated values are larger than the observations, which may also be caused by the inputs of the biodegradation rate constants being smaller than experimental data. For example, an input biodegradation rate constant of 1.3/day, which is in the range of the majority of lab studies in the 3MRA database, would lead to a correct computed effluent concentration for phenol.

Overall, the modeling study using the combined LAU and VZ modules overestimates the effluent concentration for halogenated aliphatic hydrocarbons, which are highly volatile and not easily biodegradable in aerobic conditions, but provides good estimations for substituted benzenes, which undergo significant volatilization and biodegradation. Given the correct inputs of biodegradation rate constants, it could produce correct results for phenols, which has little vaporization and significant biodegradation.

Findings and Suggestions on Model Applications

The following present the findings from this model evaluation. First, it is appropriate to utilize the Lab data of the GWERD large soil column study in evaluating the LAU and VZ modules since the experimental design and conditions were sufficiently close to the assumptions and application conditions of the LAU and VZ modules. Second, overall, the volatilization rate modeled by the LAU program is in the right order of magnitude for all categories of compounds involved in the experiment, although the simulated volatilization is consistently lower than the observation for highly volatile organic compounds. Third, sensitivity analyses indicated that the model outputs of the LAU module show minor sensitivity to changes in thickness of the LAU module layer and temperature for most chemical compounds examined in this study. Fourth, generally the VZ model functioned quite well in simulating the fate and transport of organic constituents in vadose zones, although a noticeable difference between the simulated and observed results was observed for highly volatile organics. Fifth, evaluations conducted showed that the VZ and CHEMFLO models reached compatible results. Finally, the overall final outputs through both the LAU and VZ modules gave a good estimate of leachate concentration for organics undergoing both volatilization and transformation, while they overestimated for organics with high volatility and low transformation rate.

Based on these evaluation results, we suggest the following in order to enhance appropriate applications of the 3MRA model: 1) Perform integrated and sequential implementations of the LAU and VZ modules; 2) Reduce the uncertainty of simulation results by determining chemical transformation rates properly in the VZ module; 3) Understand the potential errors of the volatilization estimation and the leachate concentration from the LAU module for highly volatile organic compounds; 4) Pay less attention to the effects of thickness and temperature parameters in applications of the LAU module; and 5) Understand the differences between the model assumptions and site conditions, and the effect of those differences on the accuracy of model simulations.

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Disclaimer

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